ДЕФЕКТЫ КРИСТАЛЛИЧЕСКОЙ РЕШЁТКИ

The 'Particle Weighting' Effect in the Heat Capacity Temperature Dependence of the V_2D Ordering Interstitial Alloys

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As known, the local-oscillation frequencies of light atoms in the ordering interstitial V_2D alloy are temperature dependent; they decrease with temperature lowering. This effect is ascribed to the 'effective weighting' of interacting D particles in the ordered phase. The aim of this article can be formulated as an attempt to estimate the influence of this 'ordering-induced temperature-dependent weighting of light particles' on the heat-capacity−temperature dependence for a given compound.

Key words: interstitial alloys, particle−particle interactions, local-oscillation frequencies.

Відомо, що в упорядковному дейтериді V_2D частоти локальних коливань легких D-атомів залежать від температури. Цей ефект було приписано «ефективному поважчанню» частинок D, що взаємодіють в упорядкованій фазі. У даній роботі зроблено спробу оцінити вплив температурно залежних частот локальних коливань легких атомів на температурну залежність тепломісткости даної сполуки.

Ключові слова: стопи втілення, міжчастинкові взаємодії, частоти локальних коливань.

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Известно, что в упорядочивающемся дейтериде V_2D частоты локальных колебаний лёгких атомов D зависят от температуры. Этот эффект был приписан «эффективному утяжелению» частиц D, взаимодействующих в упорядоченной фазе. В настоящей работе сделана попытка оценить влияние температурно зависимых частот локальных колебаний лёгких атомов на температурную зависимость теплоёмкости данного соединения.

Ключевые слова: сплавы внедрения, межчастичные взаимодействия, частоты локальных колебаний.

1. INTRODUCTION

In the V_2D compound, the metal atoms (M atoms) form a b.c.c. lattice. The light deuterium atoms (D atoms) are located in the octahedral interstitial positions of the metal lattice. The total number of the octahedral interstitial positions can be represented as three interpenetrated b.c.c. sublattices. In the high-temperature disordered state, the D atoms are distributed randomly on the set of all octahedral positions, while, in the low-temperature ordered state, they are concentrated in one of these three sublattices and form an ordered configuration. The order−disorder transition occurs at $T_{tr} = 406$ K.

The thermal excitations of M atoms are represented by the acoustic waves in the metal lattice with the frequencies in the range $[0 - \nu_{max}]$ and are characterized by the Debye temperature T_{Deb}. The thermally excited interstitial light atoms oscillate separately and are characterized by two different frequencies illustrated in Fig. 1: for the displacements along the vertical *c*-axis (the high-frequency oscillations— HF-oscillations) and for the displacements within the horizontal *ab*-
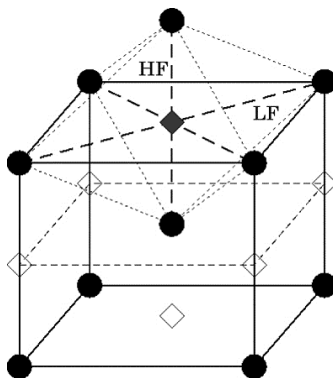

Fig. 1. The crystal lattice of the ordering V_2D alloy. Black circles—vanadium atoms, open rhombus—the sites of the b.c.c. sublattice of the octahedral interstitial positions accessible for the deuterium atoms in the ordered phase.

plane (the low-frequency oscillations—LF-oscillations). They are characterized correspondingly by two different Einstein temperatures—$T_E(LF)$ and $T_E(HF)$.

It has to be noted that the local oscillations of the light atoms can be characterized by the corresponding energies $E(i)$, the frequencies $\omega(i)$ and the Einstein temperatures $T_{E(i)}$. These parameters are related by the simple relations:

$$E(i) = (h/2\pi)\omega(i), \ \ E(i) = k_B T_{E(i)} \ (i = 1, 2), \tag{1}$$

where $i = 1$ and $i = 2$ correspond to the low frequency (LF) and the high frequency (HF) modes, respectively.

Some decades ago, basing on the inelastic neutron diffraction experiment, J. M. Rowe had established [1] that, in the ordering V_2D compound, the energies of both oscillation modes decrease significantly below the order—disorder transition point $T_{tr} = 406$ K. It was registered, particularly, that, at $T = 425$ K (*i.e.*, at $T > T_{tr}$),

$$T_{E(1)} \equiv T_E(LF) = 936 \text{ K}, \ \ T_{E(2)} \equiv T_E(HF) = 1408 \text{ K}, \tag{2a}$$

while, at 300 K (at $T < T_{tr}$),

$$T_{E(1)} \equiv T_E(LF) = 561 \text{ K}, \ \ T_{E(2)} \equiv T_E(HF) = 897 \text{ K}. \tag{2b}$$

The unexpected experimental results [1] were explained [2] on assuming that the registered frequency lowering was provided by the 'weighting' of the light oscillating particles due to the additional D—D bonds formed in the ordered state.

It seems obvious that the changes of the local-oscillation frequencies must be reflected in a total heat capacity $C(T)$ of an interstitial alloy. The latter contains the heat capacity parts associated with the thermal excitations of the acoustic waves in the metal lattice—$C_{ac}(T)$, with the local oscillations of the light atoms—$C_{opt}(T)$, with the ordering of light atoms—$C_{ord}(T)$, and with the excitation of conduction electrons—$C_{el}(T)$. Thus, for the compound V_2D, we can write:

$$C(T) = C_{ac}(T) + C_{opt}(T) + C_{ord}(T) + C_{el}(T). \tag{3}$$

In the article [3], we had roughly estimated the temperature dependence of the total heat capacity of the V_2D compound on assuming that, at temperatures $T > T_{tr}$, the local mode frequencies are equal to the values (2a), while, in the whole temperature range $T < T_{tr}$, the local mode frequencies are equal to the values (2b). We had shown that these changes in the local mode frequencies can be reflected in the summary heat capacity of the sample.

Subsequently, we had considered [4] the quantum model of a D oscillator interacting with the neighbouring D particles, and we had described the corresponding perturbation by the additional potential V_{DD}.

In the present article, we intend to estimate in more details the influence of the temperature dependent frequencies of local oscillators on the total heat capacity of the V_2D compound.

2. MATHEMATICAL DETAILS

2.1. General Conditions

The motions of particles in the interstitial solid solution V_2D are characterized by the following energy parameters: the Debye temperature T_{Deb} (for the acoustic waves in the metal lattice) and the Einstein temperatures $T_E(i)$ (for the local—'optical'—oscillations of the interstitial atoms).

The subsystem of conduction electrons has its part in the total heat capacity of the sample. It depends on the density of states at the Fermilevel and is characterized by the corresponding constant g_{el}.

T_{Deb} depends significantly upon the inter-atomic distances in the metal lattice. The introduction of light interstitial particles influences upon the interatomic distances between the vanadium atoms. It means that $T_{Deb}[V_2D] \neq T_{Deb}[V]$. We have used below the value of T_{Deb} determined for the 'pure vanadium lattice'.

The interstitial deuterium atoms influence as well on the system of the conduction electrons and will generally change their part in the total heat capacity of the sample, *i.e.*, $g_{el}[V_2D] \neq g_{el}[V]$. We have assumed nevertheless that both these constants are approximately of the same magnitude.

For both these reasons, the numerical results given below have to be considered only as the qualitative preliminary data and have to be corrected basing on the precise heat capacity measurements performed directly on the V_2D sample.

2.2. Temperature Dependence of the Local Oscillator Frequencies

It was shown [4] that the temperature dependence of the local oscillator frequencies in the given metal lattice can be presented as

$$\omega_{(i)}(T) = \omega_{(i)}(0)f_{(i)}(T) \ (i = 1, 2), \tag{4}$$

where

$$\omega_{(1)}(T) \equiv \omega_{(LF)}(T) \text{ and } \omega_{(2)}(T) \equiv \omega_{(HF)}(T),$$

while

$$f_{(i)}(T) \equiv [1 - V_{DD}(T)/E_0(i)]^{-1}. \qquad (5)$$

Here, $\omega_{(i)}(0)$ and $E_0(i)$ are the oscillators' frequencies and energies at temperatures higher than the order–disorder transition point T_{tr}, and $V_{DD}(T)$ is the temperature-dependent potential perturbing the local oscillators at temperatures below the temperature T_{tr}.

Taking into account that, at $T < T_{tr}$, the subsystem of D particles is characterized by the nonzero ordering energy $E_{ord}(T)$, we had assumed that, in the system of N metal atoms containing N_D interstitial deuterium atoms, the perturbing potential V_{DD} is proportional to the $(1/N_D)$ part of the ordering energy $E_{ord}(T)$ (i.e., to the part of the ordering energy per single D particle):

$$V_{DD}(T) = bE_{ord}(T)/N_D. \qquad (6)$$

Here, b is a numerical parameter estimated basing on the experimental data [1], while $E_{ord}(T)$—'the ordering energy'—is the calculated value of the energy associated with the formation of the ordered spatial configuration of the interstitial D particles. In order to determine $E_{ord}(T)$ numerically, we have to repeat shortly the sequence of the steps considered already in [4] (see below).

2.3. The Ordering Process in the Subsystem of Deuterium Atoms

The D atoms inserted in the vanadium b.c.c. lattice occupy the octahedral interstitial positions (see Fig. 1). The total set of octahedral positions in the b.c.c. metal lattice can be presented as three interpenetrating b.c.c. sublattices. In the disordered phase of the V_2D compound, the light atoms are distributed randomly on the set of all octahedral interstitial positions, while in the ordered phase the interstitial D atoms are collected in one of these three sublattices and at the sites of this sublattice form a spatially ordered configuration described by a temperature-dependent order parameter $\eta(T)$ (see, e.g., Refs. [4, 5]).

The analytical expression of $E_{ord}(T)$ can be written basing on the static concentration waves model formulated by A. G. Khachaturyan [5]. In the case of the system under consideration, it looks like [4]

$$E_{ord}(T) \equiv E(\eta(T), c) = (1/2)Nk_B[V(\mathbf{0})c^2 + V(\mathbf{k}_1)(\eta(T)\gamma)^2], \qquad (7)$$

where $V(\mathbf{0})$ and $V(\mathbf{k}_1)$ are the Fourier components of the D-particles' interaction energy [5, 4], $\gamma = 0.5$ is the normalizing factor and $\eta(T)$ denotes the equilibrium at the temperature T value of the order parameter η.

The first term in (7) is temperature independent, while the second one contains the temperature-dependent parameter $\eta(T)$ and includes a constant $V(\mathbf{k}_1)$, which is related to the order−disorder-transition temperature,

$$T_{tr} = -V(\mathbf{k}_1)c(1-c),\qquad(8)$$

that makes it possible to determine numerically the energy parameter $V(\mathbf{k}_1)$ basing on the experimentally determined order−disorder-transition point T_{tr}.

For these reasons, it is convenient to present the expression (7) as

$$E_{ord}(T) = E(c) + E(T),\qquad(9)$$

where

$$E(c) = (1/2)Nk_B V(0)c^2,\qquad(10a)$$

$$E(T) = (1/2)Nk_B V(\mathbf{k}_1)(\eta(T)\gamma)^2.\qquad(10b)$$

The heat-capacity part associated with the ordering subsystem depends only on $E(T)$ given by (10b), where the 'equilibrium order parameter' is determined as the value $\eta(T)$ that provides the minimum of the free-energy function of the ordering subsystem, $F(\eta, c, T)$, at the given temperature T. This condition implies a fulfilment of the equation $\partial F/\partial T = 0$, which, in the case of the V_2D compound, looks like [4] as follows:

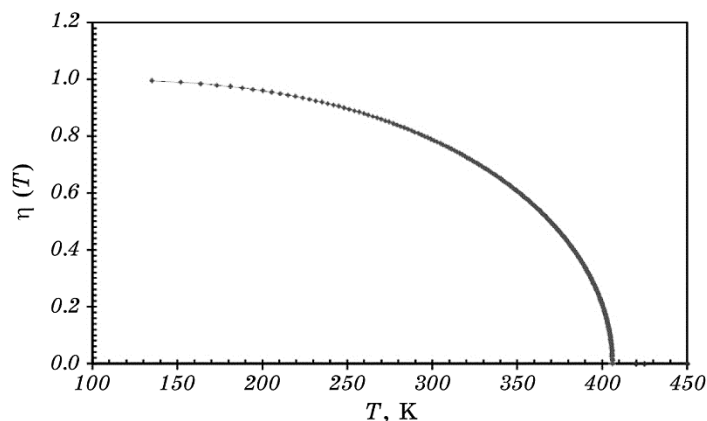$$\ln[n_1(1-n_2)/(n_2(1-n_1))] = -(V(\mathbf{k}_1)/T)\eta,\qquad(11)$$

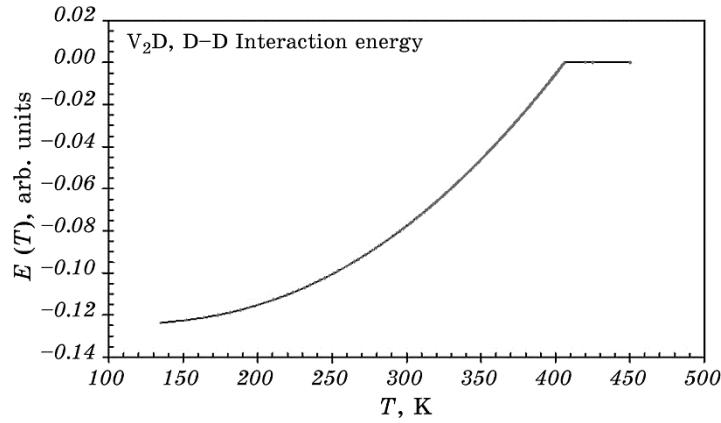Fig. 2. The temperature dependence of the equilibrium order parameter $\eta(T)$.

Fig. 3. The temperature dependence of the ordering energy $E(T)$.

where n_1 and n_2 are the sites occupation numbers in one of the b.c.c. sublattices of the octahedral interstitial positions. Particularly, in our case, we have [4]:

$$n_1(T) = c + \eta(T)\gamma, \quad n_2(T) = c - \eta(T)\gamma. \tag{12}$$

As in the given case $c = 0.5$, $\gamma = 0.5$ and the order parameter changes within the range $0 \le \eta(T) \le 1$, from (12), it follows the physically conditioned restrictions:

$$0.5 \le n_1 \le 1, \quad 0.5 \ge n_2 \ge 0. \tag{13}$$

Solution of Eq. (11) with respect to the variable η can be performed only numerically, but from the same expression (11), it can be determined the analytical dependence of the temperature corresponding to the given value of the order parameter η:

$$T(\eta) = -V(\mathbf{k}_1)\{\eta/\ln[n_1(1 - n_2)/(n_2(1 - n_1))]\}. \tag{14}$$

This makes it possible to construct the $\eta(T)$ dependence and to determine the temperature-dependent part $E(T)$ of the ordering energy $E_{\mathrm{ord}}(T)$. The corresponding dependences are shown in Figs. 2 and 3, respectively.

2.4. The Temperature Dependence of the Local Oscillation Frequencies

Basing on the expressions (4)–(6) and the calculated results shown in Fig. 3, we can determine the normalized temperature dependence of
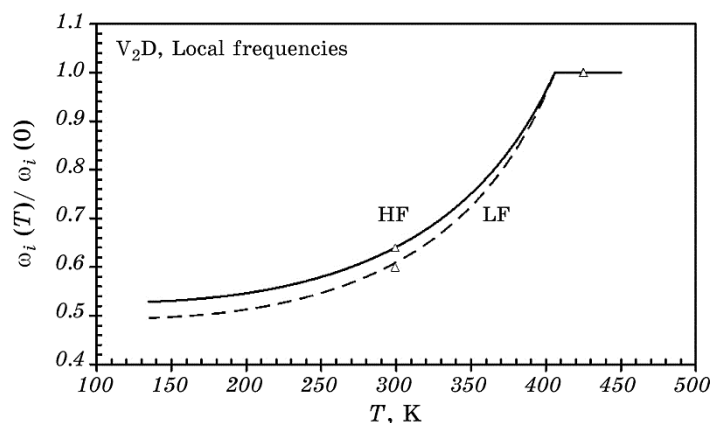
Fig. 4. The temperature dependence of the local oscillation frequencies based on the expressions (4)–(6), (9), and (10b).

both local-mode frequencies (*i.e.*, the temperature dependence of the ratio $[\omega(i)(T)/\omega_0(i)]$).

The suitable values of the normalizing parameters $b(i)$ are determined from the condition of coincidence of the calculated and experimental data at 325 K. The final results of the frequencies' temperature dependence calculations are shown in Fig. 4. It is significant to note that the selected values of both parameters, $b(\text{LF})$ and $b(\text{HF})$, are different:

$$b(\text{LF}) = 4.74, \quad b(\text{HF}) = 6.25. \tag{15}$$

Basing on this difference, it can be concluded that, in the case of the ordered configuration of the surrounding D atoms, their influence on the oscillations of the given D atom is different for its displacement in the different directions.

3. THE HEAT CAPACITY COMPONENTS EXPRESSIONS

3.1. The Local Oscillations of D Atoms

We consider the set of cN D atoms inserted in the lattice of N metal atoms (M atoms) corresponding to 1 mole of the MD_c compound.

The quantum oscillator of frequency ν at temperature T has a Planck mean energy:

$$\varepsilon_\nu = h\nu\{\exp[z(T)] - 1\}^{-1}, \quad z(T) \equiv h\nu/(k_B T). \tag{16}$$

The heat capacity of cN oscillating deuterium atoms is described by

the Einstein relation [6]:

$$C_{opt}(T) = c3R_0[z_E(T)]^2\{\exp(z_E(T))/[\exp(z_E(T)) - 1]^2\}, \tag{17}$$

$$z_E(T) \equiv T_E/T, \tag{18a}$$

$$R_0 = Nk_B \approx 2 \, [\text{cal/mole·K}]. \tag{18b}$$

3.2. The Acoustic Waves in the Lattice of N Metal Atoms

The corresponding heat capacity part of the given compound is described (within the Debye approximation) by the expression [6]

$$C_{ac}(T) = 3R_0\{3(T/T_{Deb})^3 \int_0^{z_M} \{[z]^4 \exp(z) / (\exp(z) - 1)^2\}dz, \tag{19}$$

where

$$z_M \equiv T_{Deb}/T, \tag{20a}$$

$$T_{Deb} \equiv h\nu_M/k_B. \tag{20b}$$

T_{Deb} is the 'Debye temperature' estimated [5] from the experimental data.

3.3. The Subsystem of Conduction Electrons

This heat capacity part is represented by the expression [6]

$$C_{el}(T) = g_{el}T, \tag{21}$$

where the factor g_{el} is related to the number of conduction electrons n_e or (more precisely) to the density of electronic states at the Fermi level $n(E_F)$. As we have mentioned above, we have assumed that $g_{el}(V_2D) \equiv g_{el}[V]$. In the review [6], the parameter $g_{el}[V]$ was estimated basing on the experimental results.

3.4. The Ordering Subsystem of Deuterium Atoms

The heat capacity part associated with the ordering process can be defined as

$$C_{ord}(T) = [E(T + \Delta T) - E(T)]/\Delta T, \tag{22}$$

where the ordering energy of D particles $E(T)$ is given by the expres-

sion (10b) and is represented in Fig. 3.

3.5. The Set of the Used Numerical Parameters

The numerical results presented below are based on the following set of parameters: $b(\text{LF}) = 4.74$, $b(\text{HF}) = 6.25$;

$$T_{\text{Deb}} = 273 \text{ K}, \ T_{\text{E}(1)}[T > T_{\text{tr}}] = 936 \text{ K}, \ T_{\text{E}(2)}[T > T_{\text{tr}}] = 1408 \text{ K},$$

$$g_{\text{el}} = 0.0021104 \text{ [cal/(mole·K}^2)], \ V(\mathbf{k}_1) = -1624 \text{ K.} \tag{23}$$

4. RESULTS OF CALCULATIONS

First of all, let us consider the influence of the ordering induced 'weighting of the ordered D particles' on the corresponding part of the heat capacity. The results of calculations based on the expressions (16)–(18) are shown in Fig. 5, where the solid curves d and f represent the low-frequency (twice degenerate) and high-frequency (non-degenerate) heat-capacity parts of the 'non-perturbed D oscillators', respectively, while the d' and f' sequences of points illustrate the 'weighting-effect' influence on the corresponding temperature dependences.

In the same temperature range, there exist other ingredients of the sample heat capacity shown in Fig. 6. They are caused by the acoustic waves in the metal lattice (expressions (19)–(20), the curve c), by the
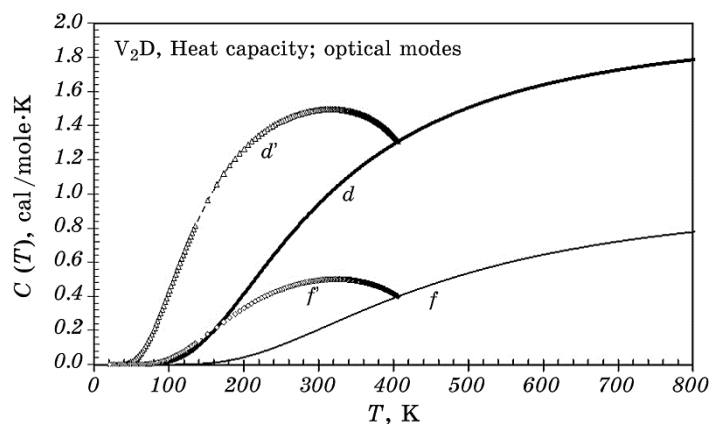

Fig. 5. The temperature dependence of the heat-capacity parts associated with the local modes. The d and f curves denote the low-frequency (LF, twice degenerate) and high-frequency (HF, non-degenerate) oscillation parts of the 'unperturbed' oscillators, respectively, while d' and f' denote the same dependences modified with taking into account the 'particles weighting' effect.
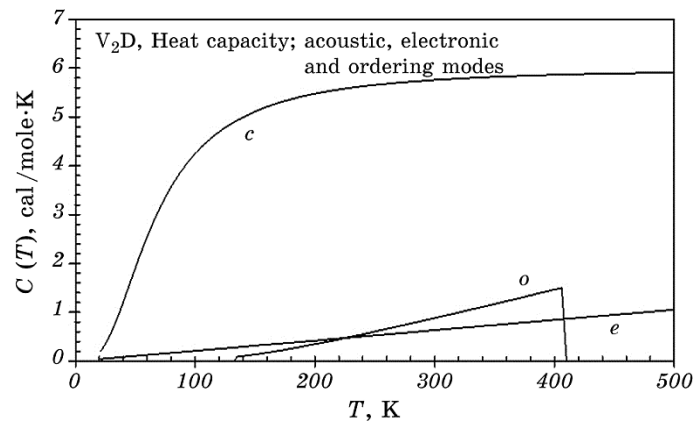
Fig. 6. The temperature dependences of the heat-capacity parts associated with the metal lattice (curve *c*), with the conduction electrons (dependence *e*), and with the ordering processes in the subsystem of interstitial particles (dependence *o*).

conduction electrons (expression **(21)**, the curve *e*), and by the ordering subsystem (expressions **(22)**, **(10b)** and **(14)**, the curve *o*).

The sum of the lattice modes is presented in Fig. 7 by the curve *l* (the unperturbed dependence) and by the curve *l'* (including the 'weighting' effect). These curves represent the sum of following components:

$$C_l(T) = C_{ac}(T) + C_{opt}(LF, T) + C_{opt}(HF, T). \tag{23}$$

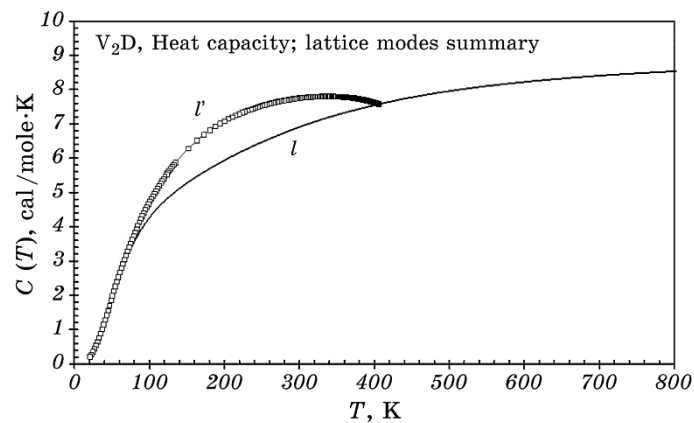Finally in Figs. 8 and 9, there are given the summary curves of the

Fig. 7. The temperature dependences of the 'lattice motions induced' parts of the total heat capacity; *l* denotes the 'unperturbed' temperature dependence and *l'* denotes the dependence, which includes the 'particles weighting' effect.
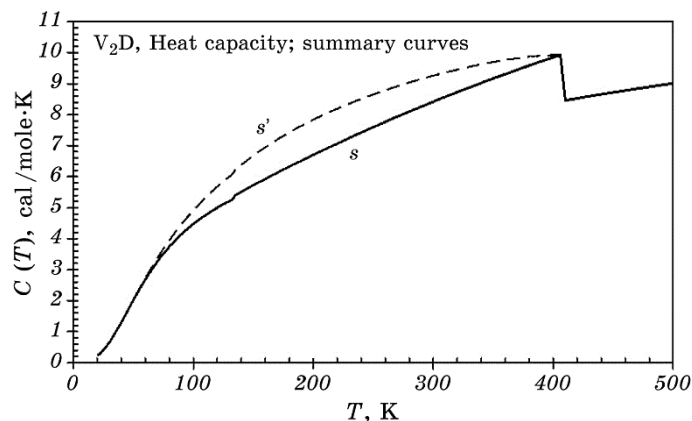
Fig. 8. The summary heat-capacity curves of the V_2D compound. s and s' denote the summary curves without taking into account the 'weighting' effect (curve s) and on taking into account this correction (curve s'), respectively.

$C(T)$ dependences for the sample V_2D denoted respectively as s and s' (Fig. 8) and the curves of their ingredients (Fig. 9). In order to avoid the uncertainties, we must indicate that, in the last two figures,

$$C_s(T) = C_l(T) + C_{el}(T) + C_{ord}(T), \tag{24}$$

where $C_l(T)$ is given by (23).

5. CONCLUDING COMMENTS

From Figures 8 and 9, it follows that in spite of the existence of differ-
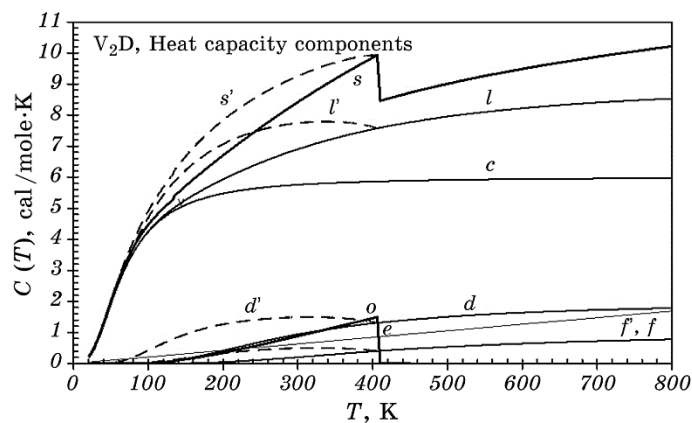

Fig. 9. The details of the summary heat-capacity curves.

ent ingredients in the total heat capacity of the V$_2$D compound the mentioned above 'weighting effect' of the oscillating particles can be registered in the heat capacity measurements. The mostly preferable temperature range for the corresponding measurements is 100−300 K.

It has to be stressed that the given calculated values of the summary heat capacity $C(T)$ curves have only a qualitative sense as we have used some constants determined for the 'pure' vanadium (and not for the deuterium containing sample). Particularly, the calculated components $C_{ac}(T)$ and $C_{el}(T)$ have to be reconsidered when the corresponding heat capacity measurements of the V$_2$D compound will be performed. The main attention has to be concentrated on the acoustic mode at temperatures 100−300 K and on the electronic mode at 300−500 K.

This article is dedicated to the memory of Iury Sharimanov (1947−2016), the experimentalist of the E. Andronikashvili Institute of Physics. In collaboration with R. Grossescu, he had published [7] the results of the NMR measurements of the spin-lattice relaxation time $T_1(T)$ performed on the sample NbH$_{0.89}$. In this article, for the first time, there was registered the anomaly presumably associated with the 'ordered-particles' weighting effect'. The registered anomalous behaviour of the $T_1(T)$ dependence was supposed to be related with the β−γ-phase transformation in the ordering hydrogen subsystem, but the 'underground' of the anomaly was not explained.

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